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Phase Transformation of *n*-Higher Alcohols. (I)

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Behaviors of phase transformations of 16 members of *n*-higher alcohols were investigated by a continuous powder method of X-ray diffraction. The results obtained are:

- i) α -forms of dodecanol and tridecanol appear in cooling process only,
- ii) γ -forms appear for even members only, and
- iii) α -forms of longer members behave differently in heating and cooling processes,

Considerable deviations from hexagonal symmetry are observed.

The transformation schemes were discussed in relation to the stabilities of correlated forms.

INTRODUCTION

The transformations between low and high temperature forms of *n*-paraffins were investigated by Müller¹⁾²⁾. According to him, the low temperature form gives two strong lines in X-ray powder pattern, while the high temperature form, which is stable in a narrow temperature range right below the melting point, gives only one strong line, indicating its hexagonal or nearly hexagonal structure. The transition between those forms is continuous in members shorter than tetracosane, while it is discontinuous in longer members. To explain the hexagonality of the high temperature form, Müller presented a model of crystal in which the molecules are rotating around their long axes. Since then, many workers investigated the rotational motion of long chain molecules in crystals by means of dielectric measurement³⁾⁴⁾⁵⁾ and recently by means of nuclear magnetic resonance⁶⁾. Though the results of these investigations modified the model given by Müller in some respects, they did not give any definite conclusion for lack of detailed knowledge concerning the crystalline structure.

Of course, the materials used for the dielectric measurements were not paraffins but their derivatives with polar groups such as ketones, acids and alcohols. Among them, *n*-higher alcohols showed very delicate behaviors¹⁾⁵⁾ probably because of the abnormal conductivities due to proton transfer and because of their complicated polymorphism.

So far, three forms have been found in *n*-higher alcohols⁷⁾⁹⁾; α is high temperature form, and β and γ are low temperature forms. The transitions among these forms have been investigated in various ways, but some of the results do not coincide with each other.

By X-ray method, Kolp and Lutton⁹⁾ found that the transition, $\alpha \rightarrow \gamma$, was irreversible, which, on the contrary, had been reported by other workers to be reversible (Phillips¹¹⁾, Meyer¹²⁾). By thermal analysis, Phillips and Mumford¹¹⁾ deter-

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mined the melting and $\beta \rightarrow \alpha$ transition points for the members from dodecanol to nonadecanol, and concluded that shorter members had no stable α -form. However they found no evidence of γ -form. Kakiuchi and his coworkers⁸⁾¹⁴⁾ investigated the specific heat of hexadecanol and found two anomalies in the specific heat curve corresponding to $\beta \rightarrow \alpha$ transition and melting, but they found no evidence of γ , too. By measurement of dielectric constants, Smyth and his coworkers⁴⁾ reported that dodecanol had no α -form on both heating and cooling, while Bernal¹⁵⁾ (by microscopic observation) and Andrew⁶⁾ (by nuclear magnetic resonance method) reported that that dodecal had α -form. Smyth⁴⁾ also explained the anomalous dielectric behavior of hexadecanol at higher temperatures to be due to Maxwell-Wagner effect for the coexistence of conducting α -form with nonconducting γ -form. But Asai⁸⁾ concluded that it is likely due to the electrode impedance which originates from the anomalous charge distributions close by the electrodes.

It seems that it is difficult to give proper explanations for such complicated phenomena without accurate knowledge of the polymorphism. The present work was attempted to clarify the polymorphic behaviors of n -higher alcohols, and to give fundamental data for the discussions on the properties of these materials.

NOMENCLATURE

Throughout the present work, solid forms of n -higher alcohols are specified by Greek letters.

α -form ; the form which is observed in a narrow temperature range below the melting point. Molecules in the form are believed to be rotating or twisting around their long axes, which are vertical to the layer plane.

β -form ; the form in which long axes of the molecules are vertical to the layer plane, but the side packing of the molecules is paraffin-like, giving two strong lines in X-ray powder pattern,

γ -form ; the form in which long axes of the molecules are tilted to the layer plane and the side packing is similar to that of β -form,

The present nomenclature corresponds to those adopted by other authors as follows.

Present paper	Kolp, Lutton	Smyth et al
α	α	α
β	sub-alpha	β_1
γ	beta prime	β^2

EXPERIMENTAL PROCEDURE : CONTINUOUS POWDER METHOD

In the analysis of ordinary X-ray powder pattern, we may dispense with the major part of the pattern except a narrow region along the intersection of the film and a plane including the incident beam. So, by recording only the part of the pattern on a film moving in the direction perpendicular to that plane, the change of crystalline structure can be observed continuously. The principle was already applied to an electron diffraction camera by Trillat and Takahashi¹⁴⁾, and to an X-ray camera for small angle diffraction by Sydow¹⁷⁾. In the X-ray diffraction, though much exposing time is required, yet it is a powerful

method for investigation of phase transformation. For the present work concerning long chain compounds, Bragg angles of almost strong lines are less than 25° and the temperatures of interest are within a comparatively narrow range near the room temperature, so an ordinary camera with flat film is enough to be used.

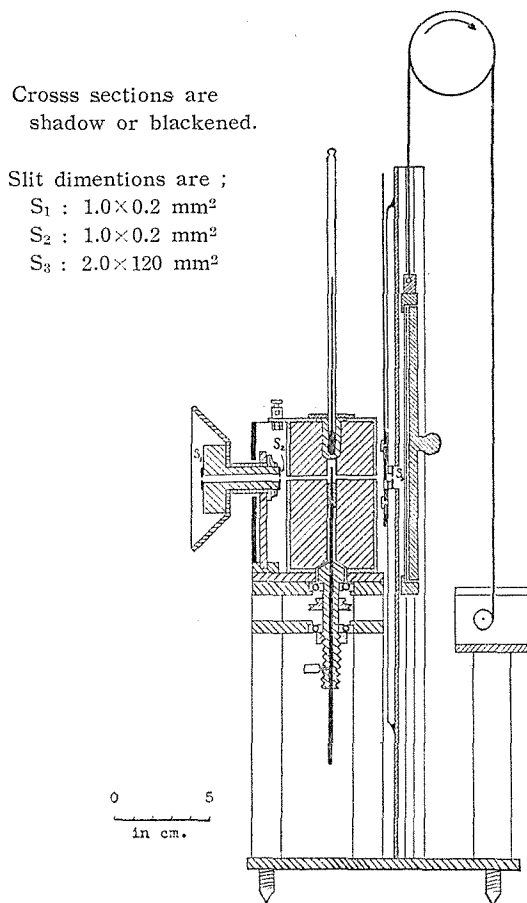


Fig. 1. Design of a camera for continuous powder method.

The design of the camera is shown in Fig. 1. The specimen is sealed off in a thin-walled glass capillary, and inserted into the hole at the top of the specimen holder. Then the holder is set at the center of the furnace. To measure the temperature of the specimen accurately, the specimen holder was carefully designed. The holder, which is made of copper, rotates contacting closely to the inside wall of the furnace, and the openings of the air are only a slit for incident beam and a canal for diffracted X-rays. Thus the specimen is not only put in an atmosphere of almost uniform temperature but can be set correctly with little adjustment. Therefore, the temperature of the specimen is much the same as that of the body of the furnace, and is measured with a thermometer or a thermocouple inserted in the upper part of the furnace. The reading of the thermometer is recorded directly on the moving film by shifting the beam stopper for a moment.

The incident X-rays come to the specimen through the slits S_1 and S_2 , and the receiving slit S_3 limits the width of the pattern recorded on the film at a time. The cassette is drawn up at a constant speed.

In our experiment using a X-ray generator with rotating anode (Ni-filtered Cu $K\alpha$, 40 KV, 25 mA, focus width 0.2 mm), the speed of the moving film was 1 mm/min. and the width of S_3 was 2 mm. These conditions were determined taking following respects into consideration.

(a) Resolution of temperature

When a phase transformation take place suddenly, the transition is recorded on the film as if it were accomplished gradually during the time corresponding to the width of the receiving slit S_3 . This will lead so an error in determination of the transition temperature, and the error is at most

$$\Delta T = \frac{\text{rate of temperature variation} \times \text{width of receiving slit}}{\text{speed of moving film}}$$

In practice, the error is smaller than ΔT . Therefore, the effect is out of question so far as the temperature varies slowly.

(b) Deformation of the line profiles

The present method is a modification of the powder method using long slits, and the profiles of diffraction lines suffered asymmetric deformation. In addition to the effect of the long slits themselves, the motion of the film has an effect similar to that of long slits on the line profiles. As a result of these effects, the apparent diffraction angles are more or less smaller than those in the ordinary Debye-Scherrer pattern, and the effect is important when small angle reflections are dealt with.

In investigation of metastable state, it is sometimes necessary to vary the temperature of the specimen rapidly, especially in cooling process. And it is desirable for the furnace to have a cooling device, which is also of use in dealing with the materials of low melting points.

MATERIALS

Materials used are 16 members of n -higher alcohol, of which carbon numbers cover from 11 to 29.

They were prepared by chemical synthesis and purified by repeated recrystallization from ethanol or benzol solution, in the Laboratory of Organic Chemistry, Kyoto University¹⁸⁾.

CRYSTAL DATA AND LONG SPACINGS

In the crystals of long chain material, molecules are generally bound side by side to make up layers. Regarding the structure of the layer, Daniel¹⁹⁾ classified the crystal structures into four classes. The first is the paraffin-like structure which is most generally observed. The second is triclinic structure which is observed in lower members of n -paraffins and triglyceride. In these two classes,

long axes of the molecules are parallel with each other. The third is cross chain configuration which is observed in K-soaps and some amides. In these crystals, chain axes are in two different directions alternatively. At low temperatures, most of the crystals have structures of the first class, and the second and the third ones are rather exceptional. The fourth is the structure of high symmetry which is considered to be due to molecular rotation. This classification is based on the concept of subcell introduced by Vand²⁰⁾, and, from this point of view, both β - and γ - forms of *n*-higher alcohols are examples of the first structure.

In the present work, though the carbon numbers of the materials cover rather a wide range from 11 to 29, strong lines in the X-ray diffraction patterns, except the long-spacing reflections, gave nearly constant spacings independent of chain length. It is clear that these constant values are due to the common periodic structure within the layers. So it is convenient to represent the side packing of molecules by a plane lattice. The constants of the two dimensional lattices reduced from observed spacings are as follows :

α -form hexagonal $a=4.81$ Å (for members shorter than eicosanol),
 β -form rectangular $a=7.33$ Å, $b=5.04$ Å,
 γ -form rectangular $a=7.34$ Å. $b=4.90$ Å.

In subcell lattice, according to Vand, *c*-axis is parallel to the long axes of the molecules, and *a*- and *b*- axes coincide respectively with *a*- and *b*-axes of the crystal lattice. In describing the subcell lattice itself, other choice of the axes may be possible. If *a*- and *b*-axes are so chosen that both of them are perpendicular to *c*-axes, which is considered to be possible for the paraffin-like structure because of the symmetry of the long zig-zag chain, the basal plane of the subcell should conform to the two dimensional lattice given above.

Long spacing, which indicates the thickness of the double layer, increases

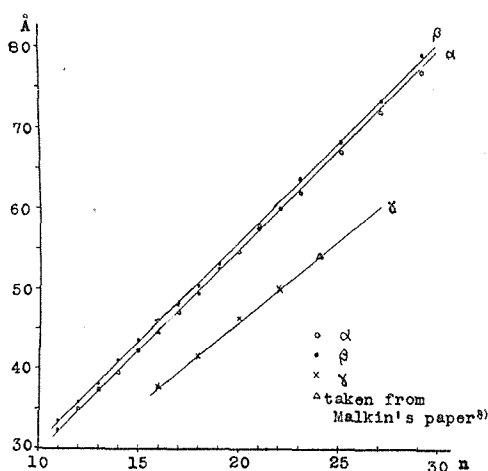


Fig. 2. Long spacing of *n*-higher alcohols.

linearly with increasing carbon numbers as shown in Fig. 2. The experimental formulae for the three forms are,

$$I_{\alpha} = 2.52n + 4.5$$

$$I_{\beta} = 2.52n + 5.5$$

$$I_{\gamma} = 2.15n + 3.2$$

Following Malkin, the tilt angles estimated from the first term are

$$\tau_{\alpha} \sim 90^{\circ}, \quad \tau_{\beta} \sim 90^{\circ} \text{ and } \tau_{\gamma} \sim 50^{\circ}.$$

Namely, molecules in α -form and β -form are vertical, while those in γ -form are tilted at an angle about 60° to the layer planes.

Another respect to be mentioned is that the long spacing of α -form is smaller than that of β -form with each member, and preceding formulae suggest that the difference should come from the inter-layer packing. As is shown in the crystal data, the cross section area per one molecule in α -form is about 10% larger than that in β -form. That is to say, in α -form, end groups in a layer are distributed less closely and the end groups of the adjacent layers would pack more closely. However, if the size of the end groups and their thermal motion are taken into account the above reason is not sufficient to explain the difference of 1 Å. This suggests that β -form may have some particular structure.

Though it has been supposed that, in general, all the polar groups in a layer are arranged on plane, they need not to be so if only the polar groups occupy their stable positions. In other words, molecules in the layer may shift alternatively

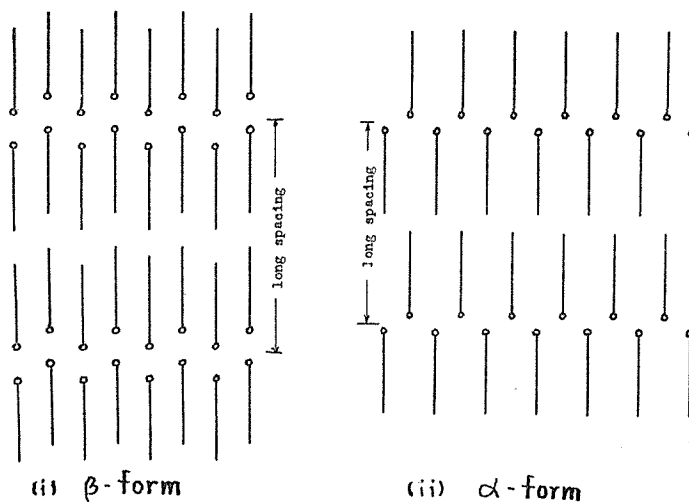


Fig. 3. Layer packing in α - and β -forms.

in the direction of their long axes, making the layer uneven (Fig. 3). If β -form of n -higher alcohols has such a structure, the long spacing is expected to be longer than α , because the uneven surface of the layer prevents the adjacent layers from coming in close contact with each other. To ascertain this assumption, of course, further analysis of the structure is needed.

ANALYSIS OF CONTINUOUS POWDER PATTERNS

The specimens were prepared in the following way. An end of a thin-walled glass capillary was dipped into the molten material to suck it up about 1 cm high.

Then the capillary was sealed off at both ends. The enclosed material was melted again and cooled at a proper rate.

In the analysis of the continuous powder patterns (which we call C P pattern hercafter), it was convenient to classify the materials into two groups, even members and odd members, according to their carbon numbers. Though shorter members, dodecanol and tridecaol, presented the same character regardless the groups they belong to, longer members presented the characteristics of the groups clearly. As the indices of reflections, those referred to subcell lattice were adopted.

(a) Odd Group

The appearance of the phase transformation in odd members bears a striking resemblance to those in *n*-paraffins, which had been reported by Müller.

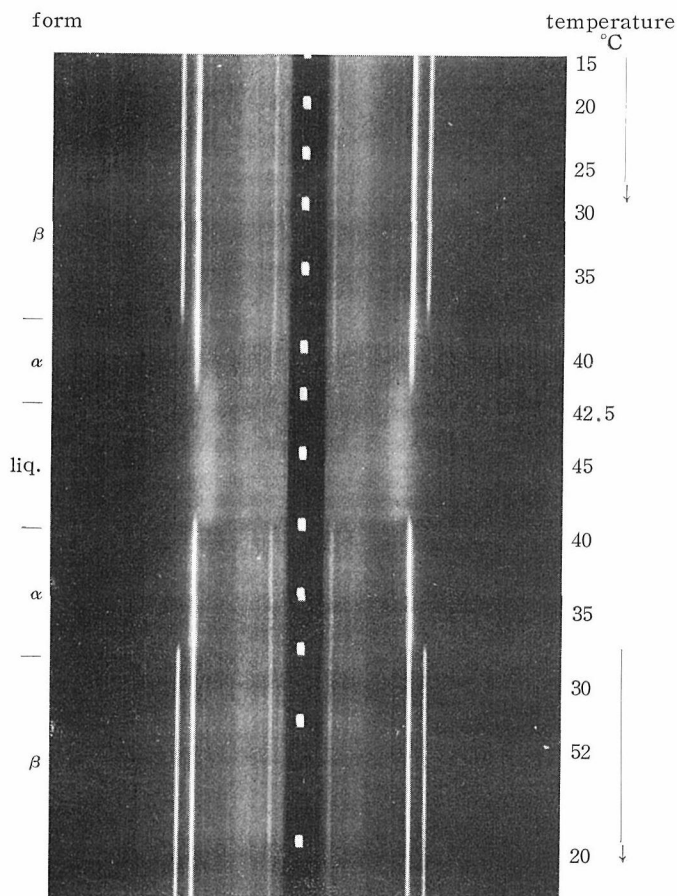
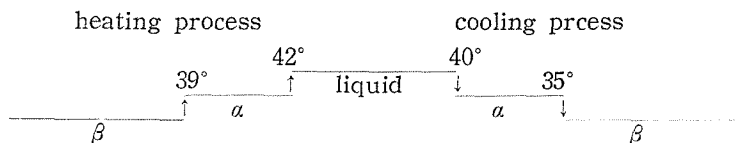


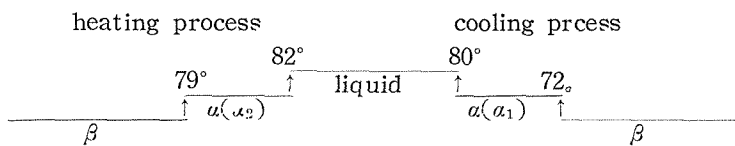
Fig. 4. CP pattern of pentadecanol $C_{15}H_{32}OH$.

(I) **Pentadecanol $C_{15}H_{32}OH$.** The C P pattern of pentadecanol is shown in Fig. 4. Several lines in small angle range are the reflections due to long spacing, and outer storog lines are due to side spacings. These lines indicate that the initial

state is purely β -form. On heating, $\beta \rightarrow \alpha$ transition takes place at 39°C and melting at 42°C . In β -region, the most strong line (110) and the second one (200) are the characteristic reflections of paraffin-like structure. In α -region two side-spacing reflections (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0) are observed. The former is very strong and somewhat diffuse, and the latter is very weak. As for the long-spacing reflections, the lines slightly shift outwards at the $\beta \rightarrow \alpha$ transition point, showing the fact discussed before that the long spacing of α is smaller than that of β . For cooling process, the change of the pattern proceeds completely backward except that (10 $\bar{1}$ 0) line of α -form is more diffuse compared with that for heating process. The above transitions are described schematically as follows :



(II) **Nonacosanol $\text{C}_{29}\text{H}_{59}\text{OH}$** . The transformations observed with nonacosanol are described schematically as follows :



The C P pattern (Fig. 5), as compared with previous one, has some complexity in α -region. Namely both (10 $\bar{1}$ 0) and (11 $\bar{2}$ 0) lines split into doublets. It seems natural to suppose that the subcell structure of α -form is no longer hexagonal but ortho-rhombic. For heating process, the spaces between the splitted lines kept nearly constant over the whole range of α -form. While, for cooling process, they varies appreciably and the lower is the temperature, the wider are the spaces, though, at higher temperatures near the freezing point, the pattern is undistinguishable from that for heating process. Thus we may conclude that there are two forms in α -region rather than one, and we designate α -forms on heating and on cooling as " α_2 -form" and " α_1 -form" respectively.

To determine the stable form in α -region, heating and cooling were repeated within the α -region. After the first transition $\beta \rightarrow \alpha$, it was once brought up to 80°C and cooled down again to 73°C . In this cooling process α_1 -form was observed. Further heating and cooling had no effect on the state of α -form. So it is sure that the stable form is α_1 and not α_2 .

(III) **Members between pentadecanol and nonacosanol**, All the members between pentadecanol and nonacosanol showed intermediate characters between the two. The splitting of diffraction lines in α -region can hardly be recognized with pentadecanol, but it becomes noticeable more and more with increasing carbon number as shown in Fig. 5.

(IV) **Tridecanol $\text{C}_{13}\text{H}_{27}\text{OH}$** . In the C P pattern (Fig. 5), α -form is observed only for cooling process. In α -region, side-spacing reflection lines are somewhat diffuse,

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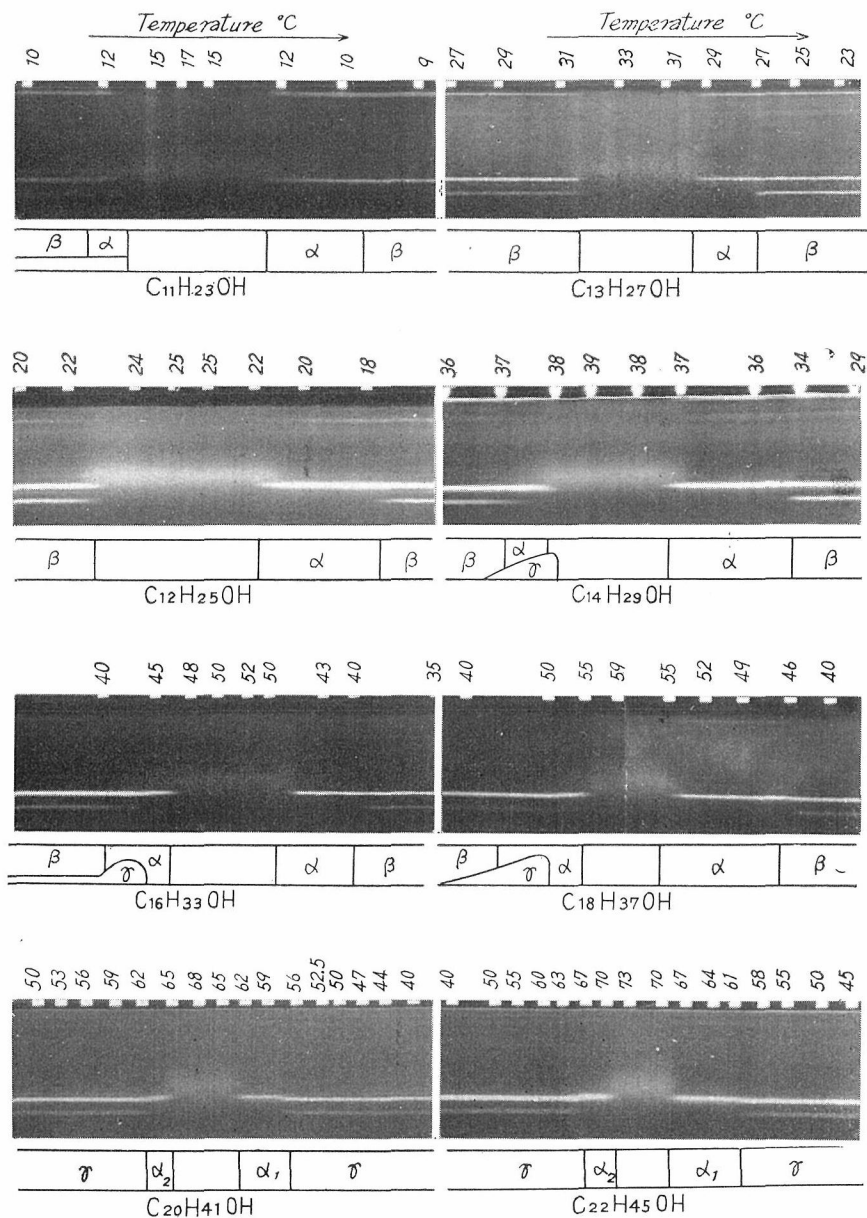
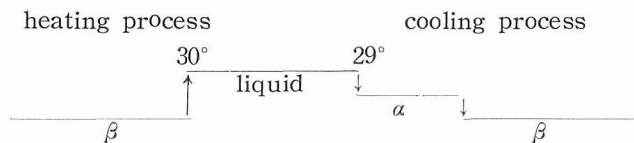


Fig. 5 (a). C. P. patterns of *n*-higher alcohols. The process were recorded from left to right.

and long-spacing reflection lines are weak compared with those of α -form. The changes observed are as follows.



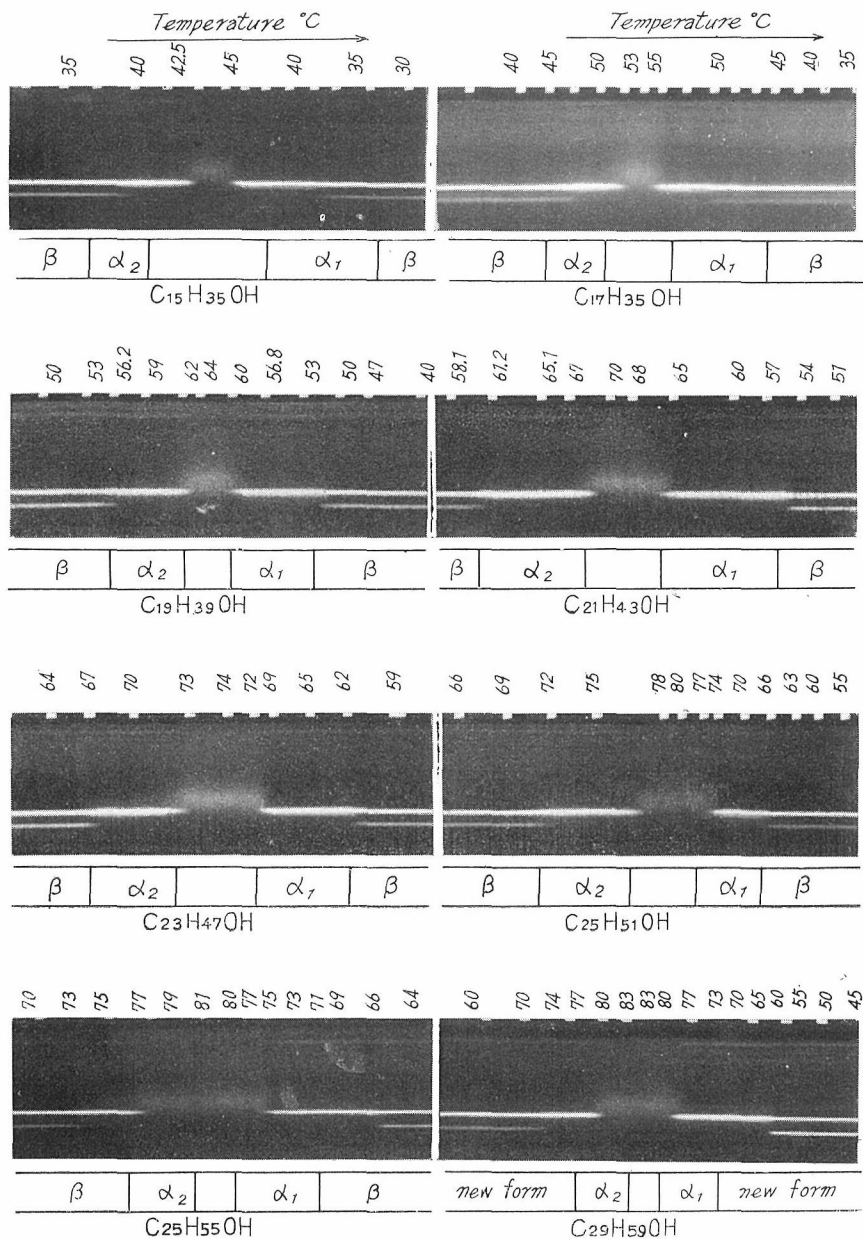
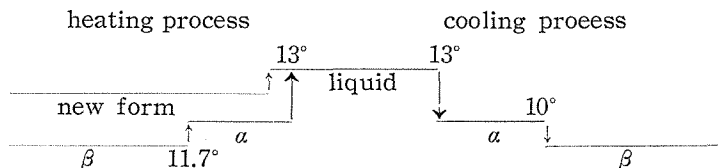


Fig. 5 (b). C. P. patterns of *n*-higher alcohols (continued). The processes were recorded from left to right.

(V) **Undecanol $C_{11}H_{23}OH$.** The specimen was prepared by dipping the melt into iced water to make the grain size small. In the first part of the C P pattern (Fig. 5) some of the side-spacing reflections are splitted into two lines respectively. The splitting is obviously due to the geometrical conditions within the specimen and of no importance. Near the strong characteristic lines, (110) and (200), of β -form, there are observed anomalous lines which are rather weak and

diffuse. Such lines are not observed with any other specimen prepared by slow cooling, and naturally, it should be due to a new form produced by chilling, though the long spacing reflections could not be observed and it is not clear whether the form had three dimensional periodicity or only two dimensional one. For heating process, the anomalous lines seem to be intensified at $\beta \rightarrow \alpha$ transition point, and lines of α -form vanish at the same time. For cooling process, no abnormality is found in the pattern because of slow cooling.



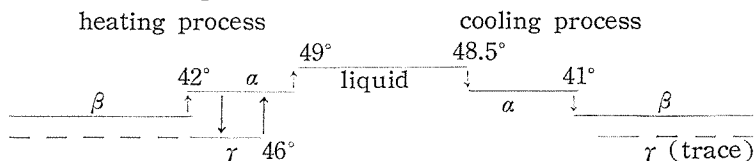
(b) Even group

Even members have two low temperature forms. To avoid confusion, they were investigated individually by an ordinary powder method. For one of them, which was identified as β , the side-spacing reflections coincide with those from β -form of odd members, and the long spacings conformed with previous expression of long spacings for β -form.

The other form is of course γ -form, and characterizes this group. The transformations in members of intermediate chain length presented the most complicated appearance.

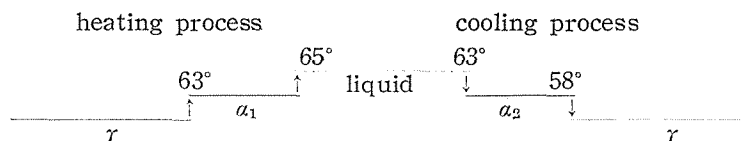
(I) **Hexadecanol $C_{16}H_{33}OH$** , The specimen was prepared by cooling the melt in the air. The first part of the C P pattern shows that the major part of the specimen was β -form. The outside of the lines of (110) and (200) reflections are diffuse which is due to the reflections from a little quantity of γ -form coexisted. For heating process, at 42° C, (200) line of β -form disappears and, instead, the corresponding line of γ -form is intensified. Though it looks as if this temperature is $\beta \rightarrow \gamma$ transition point, it can not be so, because γ -form is stable not only at higher temperatures but at room temperature. In fact, very slow cooling always produced γ -form only. Therefore, the sudden disappearance of β -form should be a result of $\beta \rightarrow \alpha$ transition. After all, the changes among the reflection lines correspond to a double transformation $\beta \rightarrow \alpha \rightarrow \gamma$. The C P pattern also shows that the γ -form changed to α at 46°C and the stable form at the melting point was α -form.

For cooling process reflection lines of γ -form are not observed in the pattern, and only a trace of γ was found in the specimen cooled down to room temperature. The schematical representation is as follows:



(II) **Octadecanol $C_{18}H_{37}OH$** , The behavior of octadecanol was similar to that of hexadecanol except that $\beta \rightarrow \alpha$ transition was observed even at low temperatures. In C P pattern, there is observed a tendency that the lines of γ -form become stronger and stronger with increasing temperature.

(III) **Eicosanol** $C_{20}H_{41}OH$ and **docosanol** $C_{22}H_{45}OH$. The C P patterns were as simple as those of odd members, but the low temperature form was γ -form instead of β -form. The transformations in eicosanol are shown below.



In the C P pattern of these materials, the (10 $\bar{1}$ 0) line of α -form is doublet and splitting is more striking for cooling process as in the case of longer members of odd group.

(V) **Tetradecoanol** $C_{14}H_{29}OH$. On heating, $\beta \rightarrow \alpha$ transition took place at 37.5°C, then α -form changed gradually into γ -form, and both α - and β -form melted at their respective melting point before the transition would be completed. On cooling, γ -form was not observed. The transformations may be described as follows :

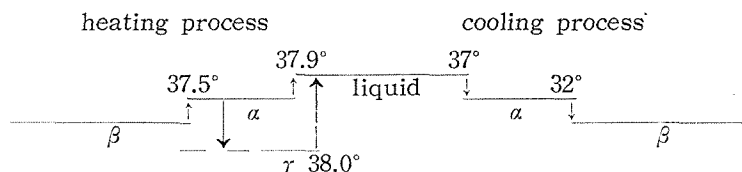


Table. Transition temperatures(in °C).

Carbon number	in heating process				in cooling process			
	T($\beta \rightarrow \alpha$)	T($\gamma \rightarrow \alpha$)	T($\alpha \rightarrow \text{liq.}$)	ΔT_h	T(liq $\rightarrow \alpha$)	T($\alpha \rightarrow \beta$)	T($\alpha \rightarrow \gamma$)	ΔT_c
11	11.7	—	13	1.3	13	10	—	3
12	—	—	23**	—	22	18	—	4
13	—	—	3**	—	29	25	—	4
14	37.5	—	38*	0.6	37	32	—	5
15	39	—	42	3	40	35	—	5
16	42	46	49	7	48.5	41	—	7.5
17	48	—	53	5	51	42	—	9
18	49	52	57	8	55	46	—	9
19	54	—	62	8	60	48	—	12
20	—	63	65	—	63	—	58	—
21	60	—	68	8	65	54	—	11
22	—	67	72	—	67	—	61	—
23	68	—	73	6	69	60	—	9
25	72	—	77	5	76	67	—	9
27	75	—	80	5	78	60	—	8
29	79	—	82	3	80	72	—	8

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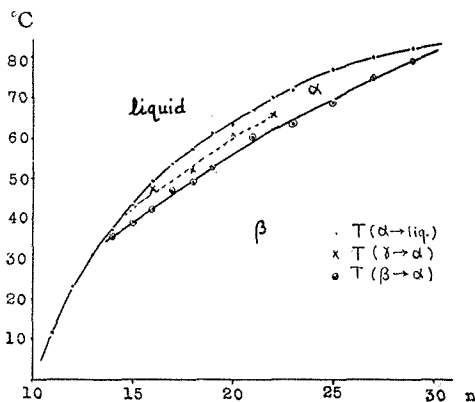


Fig. 6. Phase diagram *n*-alcohols.

(VI) **Dodecanol** $C_{12}H_{25}OH$. The transformations observed with dodecanol was similar to that of tridecanol, and γ -form was not observed.

The melting and transition points obtained by this method are tabulated in Table and also plotted in Fig. 6.

DISCUSSION

Noticeable facts observed by C P method are as follows:

- γ -form existed only in even members longer than tridecanol,
- α -form of dodecanol and tridecanol existed in cooling process only,
- α -form of longer members presented deviations from hexagonal symmetry, and the lattice constants and its temperature dependences were different according to heating or cooling process,
- except $\alpha_1 \rightarrow \alpha_2$ transition, all of the transformations observed were of first order, and the $\beta \rightarrow \alpha$ transition took place abruptly without any precursive deformation of the lattice.

In the present work, our purpose was to see what solid form exist at each temperature with each member of the series, and not to go into kinetics of the transformations. We shall discuss below the former three of the cases cited above, then touch briefly on the possibility of a new form.

(a) With odd members, γ -form was not observed at all, but it is not surprising if an ordinary alternation effect is taken into consideration. Generally, the $\gamma \rightarrow \beta$ transition point is higher than the $\beta \rightarrow \alpha$ transition point with even members. However, γ -form is a tilted form and the $\gamma \rightarrow \alpha$ transition point should be subjected to the alternation effect, so it may be lowered with odd members and the above relation between the transition points may be reversed. Under such a condition it is natural that γ -form should hardly come into existence.

Among even members, γ -form was realized more easily with longer members. Such a tendency should be attributed to the rates of transformations rather than the relative stabilities. Then crystal data show that the side packing of molecules is closest in γ -form, so it is natural to suppose that the array of the hydrocarbon chains in γ -form is most stable, and that this form is favorable to longer molecules in which hydrocarbon parts are predominant. This is consistent with the above

tendency, but does not explain the large rate of the transition into γ -form from other form in longer members. A possible reason might be found in the flexibility of long hydrocarbon chain.

To describe the transitions plainly, it is necessary to give the relative stabilities of the forms. Entropies of the three forms and the liquid will satisfy the relation

$$S_{\gamma} < S_{\beta} < S_{\alpha} < S_{liq}.$$

The behaviors of transformation reveals a schematical diagram of the thermody-

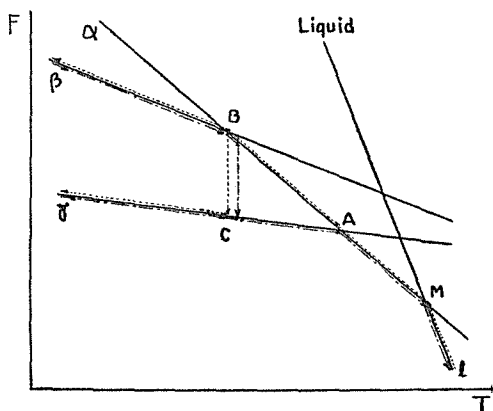


Fig. 7. Free energy diagram for even group.

namic potentials (Fig. 7). Dotted lines in the diagram corresponds to the changes observed in the C P pattern.

Thermal analysis with octadecanol give a result consistent with that from C P pattern. The heat capacity curve (Fig. 8) showed three peaks at the transition points $\beta \rightarrow \alpha$, $\gamma \rightarrow \alpha$ and the melting point. The first peak corresponding to $\beta \rightarrow \alpha$ transition was small and its shape was not reproducible. Such an abnormality it easily understood by assuming that the specimen had included both β - and γ -form. According to the result from C P pattern, $\beta \rightarrow \gamma$ transition proceeds even at lower temperatures, and especially immediately above the $\beta \rightarrow \gamma$ transition point, α -form tends to change into γ -form. Of course these transitions are exothermic and may happen occasionally. Therefore, the first peak may be small and have irregular shape.

For hexadecanol, the heat capacity showed only two peaks at the $\gamma \rightarrow \alpha$ transition point and the melting point. This mean that the specimen had included γ -form only and it seems to contradict the previous result that γ -form of longer member is realized more easily. We could find no sure reason for this contradiction except that the specimens for both methods were prepared by cooling at quite different rates.

(b) With dodecanol and tridecanol, α -form observed on cooling. On the contrary, in dielectric measurement with dodecanol, Smyth found no anomal corresponding to the existence of α -form. Asai obtained the same result as Smyth's with the very material used in the present work. For heating process, the C P pattern of

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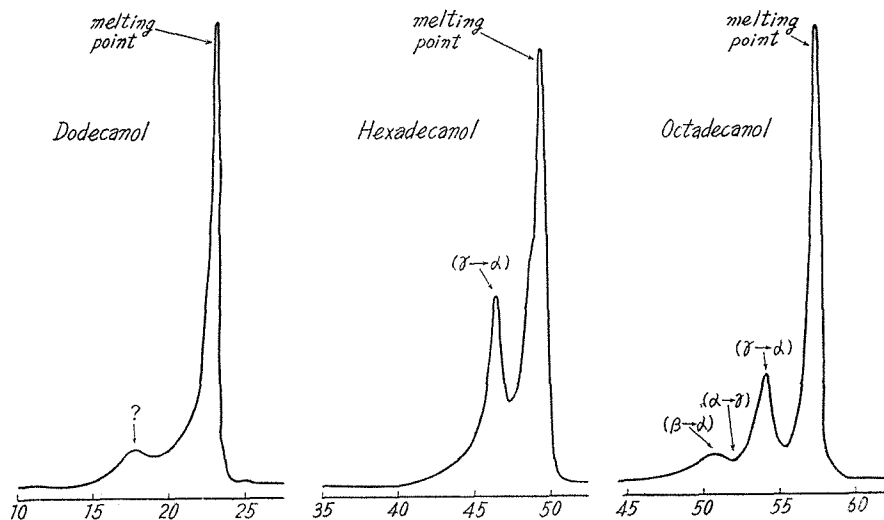


Fig. 8. Heat capacity curves of *n*-higher alcohols in arbitrary scale.

dodecanol showed no anomaly other than melting, while the heat capacity curve showed a small peak near the melting point (Fig. 8). The above inconsistency is possible because it is difficult to detect a change occurred among the polar groups by the X-ray powder method even if the change plays an important role in the thermal and dielectric properties.

The α -form of dodecanol may be considered to be metastable for the reason that the melting points of α - and β -form are nearly equal and α -form has higher entropy than β -form. Therefore, the range where the α -form remains may vary according to the rate of cooling. Even if so, the striking discrepancy between the results from the X-ray observation and dielectric measurements is hard to be explained, though there is a possibility that the molecules in the α -form of dodecanol may be combined into double molecules with little dipole moments. In any case, we may conclude that hexagonal symmetry does not always correspond with anomalous dielectric constant due to dipole orientation.

(c) The symmetry of the subcell in α -form deviates from hexagonal one with longer members, and the deviation becomes more and more striking as the carbon number increases. This means that the deviation is not due to end groups but due to a property of long hydrocarbon chain. In fact, similar structures have been found by Müller in *n*-paraffins. Therefore, the difference between the lattice constants of α_1 and α_2 might be attributed to the difference in degree of long range order of molecular orientation. If so, α_2 -form, which shows slighter deviation from hexagonal symmetry and is unstable at lower temperatures, should be a state of disorder and of high entropy as compared with α_1 -form. The degree of order corresponding to the continuous change of lattice constants of α_1 -form is likely related to that two molecular orientations different by 180° in azimuth are possible with each molecule when the plane of carbon skeleton is given.

Lastly, we shall state an observed fact which is related to a new form. As mentioned before, there was found a form of very loose packing in the chilled

specimen of undecanol, but this form might be an intermediate state between crystal and liquid. Recently, we found an anomalous behavior β -form in C P patterns. Generally, long spacing reflection lines shifted outwards at the $\beta \rightarrow \alpha$ transition point. However, for some specimens, which had been prepared by rather rapid cooling, the lines shifted inwards. As α -form gave the same long spacing in these two cases, β -form was responsible for this difference in C P pattern. The low temperature form in the latter case might be a new form which is different from ordinary β -form in stacking of layers.

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Here, we presented a new scheme mainly by the X-ray method. To understand the scheme in detail, the next investigation by a thermal analysis is proceeding in our laboratory. Further discussions will be reported later, and we desire the scheme to be examined by the workers who are interested in the subject in various ways.

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